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Strength of Chemical Bonds

Students are not generally made aware of the extraordinary magnitude of the strengths of chemical bonds in terms of the forces required to pull them apart. Molecular bonds are usually considered in terms of the energies required to break them, and we are not astonished at the values encountered. For example, the Cl_2 bond energy, 57.00 kcal mole^{-1}, amounts to only 9.46×10^{-20} cal molecule^{-1}, a very small amount of energy, indeed, and impossible to measure directly. However, the forces involved in realizing the energy when breaking the bond operate over a very small distance, only 2.94 Å, and, thus, $f_{ave} \approx D_e/(r - r_e)$ must be very large.

The following is an illustration to dramatically demonstrate the great strengths of chemical bonds compared to macroscopic concepts. Consider the homonuclear diatomic molecule $^{35}Cl_2$ whose potential energy may be represented by the Morse function

$$V(r) = 57.00[1 - e^{-2.037 \ (r-1.988)}]^2 \text{ kcal mole}^{-1} \quad (1)$$

$V(r)$ is the potential energy of the molecule and r is the bond length in Angstroms; the function is plotted in Figure 1. This bond shall be taken as comprising a representative chemical bond.

The forces involved in dissociating the molecule are discussed in the following. In consideration of average forces, the molecule shall be assumed arbitrarily to be dissociated when the atoms are far enough separated so that the potential, relative to that of the infinitely separated atoms, is reduced by 99.5% from the potential of the molecule at the equilibrium bond length (r_e) for Cl_2 of 1.988 Å; this occurs at 4.928 Å.

The force of the bond is given by

$$f(r) = -\frac{dV(r)}{dr} = -232.2[e^{-2.037(r-1.988)} - e^{-4.074(r-1.988)}],$$
$$\text{kcal mole}^{-1}\text{Å}^{-1} \quad (2)$$

The external force required to hold the bond at any given length is simply the negative of this value and the average force necessary to stretch the bond to a given length from the equilibrium length of 1.988 Å is given by

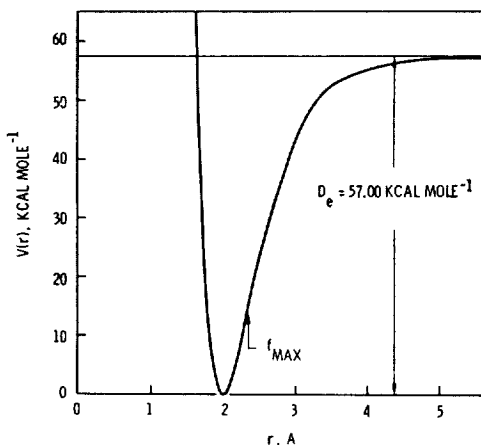Figure 1. Potential energy function plotted for the Cl_2 molecule.
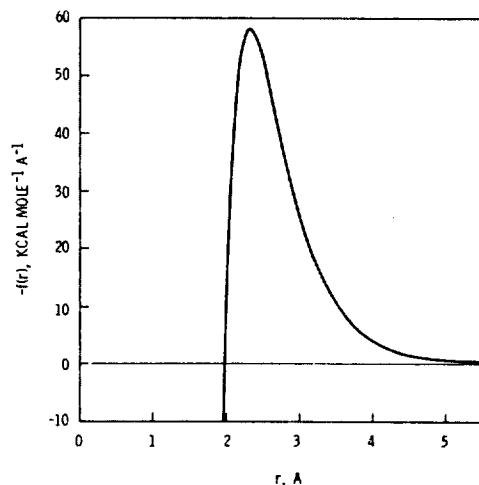

Figure 2. Force, $-f(r)$, required to stretch a Cl_2 molecule bond as a function of internuclear distance, r.

$$f_{ave} = \frac{\int_{1.988}^{r} -f(r)dr}{\int_{1.988}^{r} dr}$$
$$= \frac{232.2[-\frac{1}{2.037}e^{-2.037(r-1.988)} + \frac{1}{4.074}e^{-4.074(r-1.988)}] + 57.00}{(r-1.988)},$$
$$\text{kcal mole}^{-1}\text{Å}^{-1} \quad (3)$$

As the bond is stretched from 1.988 Å, we may see from eqn. (2) that the initial force required is zero; as the bond is stretched, a maximum force[1] of 58.1 kcal mole^{-1} Å^{-1} is reached at the inflection point of 2.328 Å and, upon further stretching, the force gradually decreases again and approaches zero as the distance becomes large. The average force required to break the bond (to stretch it to 4.928 Å) is 19.3 kcal mole^{-1} Å^{-1}. The force opposing the stretching of the bond is plotted as a function of internuclear distance in Figure 2. At distances less than the equilibrium bond length the repulsive forces in the molecule become large very rapidly.

[1] The distance and value of maximum force are calculated from the relationship

$$-df/dr = 0 = 232.2[-2.037e^{-2.037(r-1.988)} + 4.074e^{-4.074(r-1.988)}]$$

which gives the solution of $r = 2.328$ A; this may be rigorously shown to be a distance of maximum force by evaluating d^2f/dr^2 at 2.328 A and seeing that it is < 0. f_{max} is then calculated from eqn. (2) to be 58.05 kcal mole^{-1} A^{-1}.

A striking result appears when these figures are converted to values in terms of ordinary force units. Using the conversion factor 1 kcal = 94,060 cm lbs, the average force required to break a mole of Cl_2 bonds all at once is seen to be

$$\frac{19.2 \text{ kcal mole}^{-1}\text{\AA}^{-1} \times 94,060 \text{ cm lbs kcal}^{-1}}{10^{-8} \text{cm \AA}^{-1} \times 2000 \text{ lbs ton}^{-1}} =$$

$$0.90 \times 10^{-11} \text{ tons mole}^{-1}$$

and the maximum force realized is 2.73×10^{11} tons mole^{-1}. Per molecule, $f_{ave} = 0.136 \times 10^{-6}$ g molecule^{-1} and $f_{max} = 0.411 \times 10^{-6}$ g molecule^{-1}. This is a force, $0.4\mu g$, for a *single molecule*, which is macroscopically measurable!! In terms of the number of molecular masses required to exert the force, this is equivalent to 3.5×10^{15} molecules suspended from one end of a molecule with the other end held stationary.

The very great bond strengths explain why metal fibers are exceptionally strong for their sizes. The tensile strength of conventionally hard drawn tungsten is 590,000 lbs in^{-2}. Using the covalent radius 1.30 Å for tungsten, this calculates to be 0.022 μg per atomic cross sectional area, within the order of magnitude of the bond force calculated for Cl_2. The tensile strength of graphite fibers is of the order of 0.005 μg per atomic cross sectional area.

To get an even more impressive feel for the magnitude of the strength of the bond, let us expand our molecule to macroscopic dimensions. A molecule of 2 Å bond length might be thought of as 2 microbaseballs of 1 Å radius held together by a "Morse" spring (which exhibits anharmonicity when stretched). If this is compared to ordinary baseballs of, say, 3.7 cm radius, a linear increase of 3.7×10^8 times or a volume increase of 51×10^{24} times is seen. If the forces are multiplied by this factor, $0.411 \times 51 \times 10^{24}$ = 21×10^{24} μg or 23 trillion tons is obtained for the maximum force and $0.36 \times 51 \times 10^{24}$ = 6.9×10^{24} μg or 7.6 trillion tons for the average force. Thus, one might picture the pulling apart of a molecule as equivalent to pulling apart a pair of baseballs connected with a spring requiring a maximum force of 23 trillion tons to extend it. The maximum force would occur at a separation of the baseball centers of $3.7 \times 10^8 \times 2.33 \times 10^{-8}$ cm = 8.6 cm and the spring would "break"[2] at $3.7 \times 10^8 \times 4.93 \times 10^{-8}$ cm
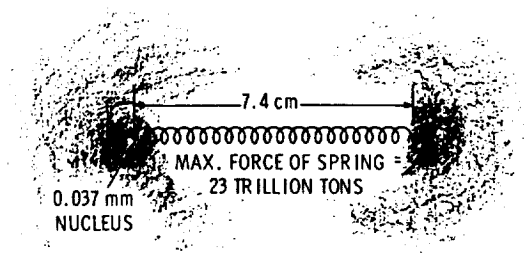

Figure 3. Depiction of a molecule of macroscopic dimensions.

= 18 cm. To be correct, the mass of the baseball should be concentrated in the center (nucleus). Since the nuclear to atomic diameter ratio for Cl is approximately $(10^{-4}\text{\AA})/(2\text{\AA})$ = 5×10^{-5}, the nucleus of each baseball atom would be ~0.037 mm diameter and would comprise practically all of the mass. The remainder of the "macroscopic" molecule would consist of approximately spherical electron clouds filling the space between the nuclei which are separated by 7.4 cm; these clouds form the very strong bond. This, then, would have the characteristics of a molecule which has been enlarged to macroscopic world size.

The "macroscopic molecule" and its properties are depicted in Figure 3.

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[2] The reader may note that the bond dissociation energy of the baseball molecule [(18.2cm − 7.4cm) (7.62 × 10^{12} tons × 2000 lbs ton^{-1}) = 1.65 × 10^{17} cm lbs or 1.75 × 10^{12} kcal)] is a factor of 1.85 × 10^{34} greater than that of the Cl_2 molecule (57.00 kcal mole^{-1} or 9.46 × 10^{-23} kcal molecule^{-1}), even though the mass (volume) ratio is only 5.1 × 10^{25}. The difference is a factor of 3.7 × 10^8, the ratio of the bond lengths. This, of course, arises because the baseball molecule bond is stretched a factor of 3.7 × 10^8 farther than the Cl_2 bond before breaking. The author feels the analogy of a spring "stiffness" of the baseball molecule being greater than that of the Cl_2 molecule by a factor of the ratio of the masses is more appropriate than the alternative choice of using the ratio of masses to the ⅔ power.